

Solid-phase photocatalytic degradation of polystyrene with TiO₂ modified by iron (II) phthalocyanine

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Abstract

A novel photodegradable polystyrene-FePc-TiO₂ (PS-FePc-TiO₂) nanocomposite was prepared by embedding the FePc-TiO₂ into the commercial polystyrene. The TiO₂ catalyst was modified by iron (II) phthalocyanine in order to improve its photocatalytic efficiency under the visible light irradiation. Solid-phase photocatalytic degradation of the PS-FePc-TiO₂ nanocomposite was carried out in an ambient air at room temperature under ultraviolet lamp and/or sunlight irradiation. The properties of composite films were compared with those of the pure PS films and the polystyrene-TiO₂ (PS-TiO₂) composite films through performing weight loss monitoring, scanning electron microscope (SEM), FT-IR and UV–vis spectroscopy. The photo-induced degradation of PS-FePc-TiO₂ composite films was significantly higher than that of the pure PS films and the PS-TiO₂ composite films both under the UV irradiation and under the sunlight irradiation. The weight loss of the PS-FePc-TiO₂ composite film reached 35% under the sunlight irradiation. FT-IR analysis and weight loss results indicated that the benzene rings in PS matrix of the composite film were cleaved during UV-light irradiation. The photocatalytic degradation mechanism of the composite films was briefly discussed.

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1. Introduction

Polystyrene (PS), poly-(vinyl chloride) (PVC) and polyethylene (PE), as the three kinds of universal plastics, are used widely in our daily life. However, the amount of waste plastics discarded is constantly increasing each year and is causing serious pollution problems where recycling may neither be available nor economically viable. The volatile of strong carcinogenic dioxins into the atmosphere from the incineration of these plastics, contained in most municipal refuse and dust particulates, is an environmental issue of major concern [1–3]. Air pollution and ground contamination in the vicinity of such small municipal facilities have become an environmental issue necessitating resolution.

The photocatalytic method represents an attractive and efficient decomposition technique for plastics by embedding

TiO₂ particles in them [4–12]. Such TiO₂-embedded PVC plastics have been investigated and the results show the composite films are degradable in open-air under UV irradiation or solar exposure [4–6]. The solid-phase photocatalytic degradation of expanded polystyrene (EPS) films with TiO₂ or modified TiO₂ as catalyst has also been reported [7–10]. In our recent studies [11], it might greatly promote the photocatalytic degradation of low density polyethylene (LDPE) film to embed TiO₂ nanoparticle in the LDPE.

Photocatalytic degradative methods for the disposal of plastics generate no dioxins and the technique is a low-temperature process with evident economic advantages. However, its technological application seems limited by several factors, the most restrictive of which is the need for an ultraviolet (UV) excitation source, which is only 3–5% of the solar beam that can reach the earth [13]. The efficient use of solar light, or other light from the visible region of the spectrum, may appear to be an appealing challenge for developing the future generation of the photodegradation plastics.

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Recently, a lot of researches are carried out to develop modified TiO₂ photocatalysts that show a high activity under the visible light irradiation in order to make the best use of the sunlight. Metal ion-implanted TiO₂ photocatalysts with various transition metals such as V, Mn and Cr ions have been investigated, which allow some photocatalytic reactions to proceed under visible light [14–17]. TiO₂ powder treated by hydrogen peroxide or chelating agent also shows higher photocatalytic activity under visible light [18,19]. TiO₂ doped with nonmetal elements such as C, N and S anions is supported to absorb visible light [20–23]. Dye sensitization of TiO₂ can extend its absorption to the visible spectral region due to the cooperative function of photosensitization and TiO₂ semiconductor in the generation of •OH radicals [24–26].

In recent years, metal phthalocyanines and porphyrins themselves or their supramolecular arrangements have been used not only in the sensor field for technological applications, but also as homogeneous or supported catalysts in a variety of oxidation reactions of organic pollutants through a biomimetic approach [27]. Indeed, phthalocyanine compounds are made soluble in a variety of solvents by appropriate peripheral substitution.

We had investigated the photocatalytic activity of TiO₂ in visible light with several dyes sensitization such as iron (II) phthalocyanine (FePc), copper (II) phthalocyanine (CuPc), cobalt octacarboxyphthalocyanine CoPc(COOH)₈, reactive blue dye (CuPz(dtn)₂SR') and iron (II) porphyrazine (FePz(dtn)₄) and tested for a probe reaction, i.e. methyl orange photo-oxidation carried out in the aqueous system [28]. Under xenon lamp irradiation, the FePc-TiO₂ composite catalyst showed much higher degradation efficiency than other experimental dyes. So FePc was chosen as the dye sensitization reagent to improve the photocatalytic efficiency of TiO₂ in this paper. A novel photodegradable polystyrene-FePc-TiO₂ (PS-FePc-TiO₂) composite film was synthesized using TiO₂ modified by FePc as photocatalyst and its photodegradation performance had been investigated. The PS-FePc-TiO₂ composite film was revealed to have much higher photodegradation efficiency under either UV light or sunlight irradiation than both polystyrene-TiO₂ (PS-TiO₂) composite film and the pure PS film.

2. Experimental

2.1. Preparation and characterization of FePc-TiO₂ photocatalysts

TiO₂ powder was Degussa P25 with 70% in anatase phase and 30% in rutile, whose primary particle diameter ranged in 30–50 nm. FePc was synthesized referring to Ref. [29]. The FePc-TiO₂ composite was prepared as follows: 1.0 g TiO₂ powder was dispersed into 50 mL ethanol solution by ultrasonic vibration for 20 min to obtain a uniform suspension. Then 50 mL FePc ethanol solution was added drop by drop into TiO₂ suspension and the weight ratio of FePc and TiO₂ was 1 and 2 wt%, respectively. The mixed solution was maintained stirring for 2 h at 343 K, then filtrated. The precipitate was washed several times with water and dried at 373 K. Finally, the FePc-TiO₂

photocatalyst was gotten. UV–vis diffuse reflectance spectra were recorded on a UV-365 spectrophotometer. X-ray powder diffraction (XRD) was carried out on a Shimadzu XRD-6000 diffractometer (Cu Kα₁, 40 kV, 30 mA) to test whether the crystalline phase of TiO₂ changed when treated by FePc.

2.2. Preparation and characterization of PS-TiO₂ and PS-FePc-TiO₂ composite films

The preparation of PS-FePc-TiO₂ composite films was cast as follows: 10 g PS was dissolved in 60 mL tetrahydrofuran (THF) under vigorous stirring for 2 h to obtain the PS solution. At the same time, 0.1 g FePc-TiO₂ powder was dispersed uniformly into 10 mL THF by ultrasonic vibration for 20 min. Then the suspension was added to PS solution to give 1.0 wt% as the ratio of FePc-TiO₂ to PS. The composite films were prepared by spreading the viscous solution on a slide glass surface (10 cm × 10 cm) and dried in airtight system for 48 h at room temperature. The pure PS films and PS-TiO₂ films were also prepared in a similar procedure in order to compare the photocatalytic activity. The thickness of these films was measured to be 40–50 μm by a micrometer. The surface morphologies of the composite samples were taken by scanning electron microscope (SEM, Hitachi X-650).

2.3. The photocatalytic degradation of PS-FePc-TiO₂ composite films

The pure films and composite films were irradiated under 30 W ultraviolet lamp (ZSZ-D, Changsha Guangming Co. Ltd.) in the ambient air. The typical surface area of the film samples was around 16 cm². The samples were placed 15 cm away from the lamp, where the light intensity was measured using a UV intensity meter (UV-I, Beijing Shida Ltd.) at primary wavelength (254 nm). The degradation extent of the films was evaluated directly by their weight loss.

The photocatalytic degradation of these films was also investigated under sunlight illumination. The 16 cm² samples were placed in the quartz vessel on a terrace in sun-shining condition from May to July, 2005, in Wuhan, China. The average exposure time was 5–8 h in 1 day. The average overall light irradiation intensity was measured using a radiometer (FZ-A, Beijing Shida Ltd.).

FT-IR spectrophotometer (JA. Transform Nicolet FT-170SX) was used to study the spectrum character of these films before and after the irradiation. The surface morphologies of all samples after irradiation for 100 h were observed by scanning electron microscope.

3. Results and discussion

3.1. The spectroscopy properties of FePc-TiO₂ photocatalysts

Fig. 1 shows the FT-IR spectroscopy of FePc, TiO₂ and FePc-TiO₂ (FePc: 1 wt%) composite powder, respectively. The characteristic IR absorption peaks of the FePc-TiO₂ composite

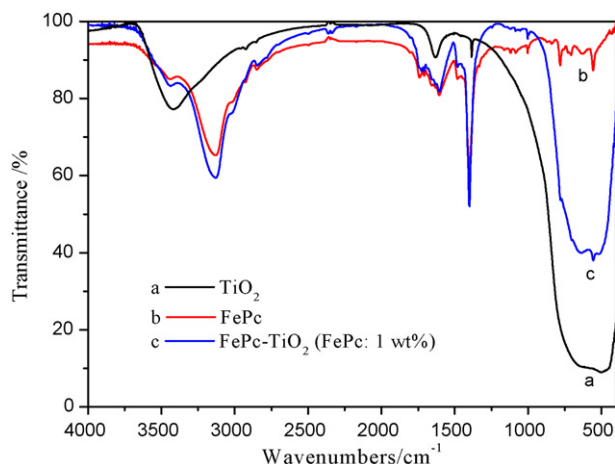


Fig. 1. The FT-IR spectra of the FePc, TiO₂ and FePc-TiO₂ composite powder (a) TiO₂; (b) FePc; (c) FePc-TiO₂ (FePc: 1 wt%).

are observed at 3136, 1600, 1400 and 530 cm⁻¹. Compared with the IR absorption spectrum of the FePc and TiO₂ powder, it shows both the characteristic IR absorption of FePc and that of the TiO₂ nanopowder around 530 cm⁻¹. It proved that the synthesized powder was the composite of FePc and TiO₂.

The UV–vis diffuse reflectance spectra of the FePc-TiO₂ (FePc: 2 wt%) composite powders are shown in Fig. 2. It is observed that the FePc-TiO₂ composite exhibits remarkable absorbance in visible region beyond 400 nm. It also shows the characteristic absorption of FePc around 730 nm.

The XRD patterns of two kinds of powder are displayed in Fig. 3. The crystalline phase of the TiO₂ catalyst is important in controlling its photocatalytic activity, and previous reports indicated that the P25 containing 70% anatase phase and 30% rutile phase displayed the best photocatalytic activity. Fig. 3 shows the size and the crystalline phase of TiO₂ have not changed through FePc modifying.

3.2. The dispersion of TiO₂ nanoparticles in PS

The dispersion of TiO₂ nanoparticles in PS was estimated by SEM (Fig. 4). It can be seen from Fig. 4a that the untreated TiO₂

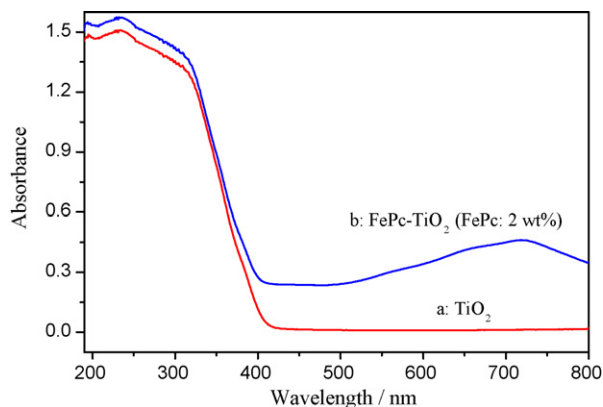


Fig. 2. The UV–vis diffuse reflectance spectra of the TiO₂ and FePc-TiO₂ (FePc: 2 wt%) powder.

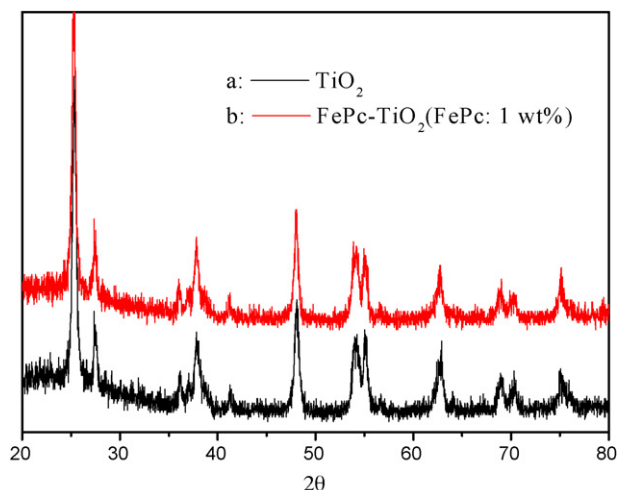


Fig. 3. X-ray diffraction patterns (Cu Kα) for TiO₂ (curve a) and FePc-TiO₂ catalyst (curve b).

aggregates seriously and has the poor dispersion in the PS polymer. However, the FePc-TiO₂ particles demonstrate a drastically different morphology in the polymer matrix (Fig. 4b). Actually, the modified nanoparticles disperse well except a few individual particles under the same instrumental setting. This result justifies that sensitized treatment of the TiO₂ nanoparticles may improve the dispersion of the nanoparticles in polymer, which can effectively enhance the photocatalytic activity of nano-TiO₂ under UV irradiation.

3.3. Weight loss analysis of the films under the different irradiations

Fig. 5 shows the photoinduced weight loss curves of the polymer films under UV irradiation in the air. The weight loss was the highest for the PS-FePc-TiO₂ (TiO₂: 1 wt%) film in the three kinds of films. The weight loss of PS-FePc-TiO₂ film steadily increased with irradiation time and reached the total 65 and 82% reduction after irradiation for 480 h under the UV light intensity for 1 and 2 mW/cm², respectively. While that of the PS film reduction was only 21 and 25%, the PS-TiO₂ film reduction was 30 and 52%, respectively, under the identical experimental condition. The results also indicated that the photocatalytic degradation of the polymer films increased with the light irradiation intensity increasing. But the weight loss of PS-FePc-TiO₂ film was much higher in low light intensity than the PS-TiO₂ film comparing with high light intensity.

The effect of water vapor on the degradation rate was investigated in humidified air. When the light intensity was 1 mW/cm², the weight loss of the PS-FePc-TiO₂ film led to 65.6% reduction in an abundance of water vapor (humidity: 95%) (Fig. 6), while that was only 22.4% in dry air (Fig. 5) after 192 h irradiation. It has been widely recognized that water adsorbed in the surface is important in catalytic process of TiO₂. Our results agree with this. It seems reasonable to assume that physically adsorbed water is vital to the decomposition of PS film.

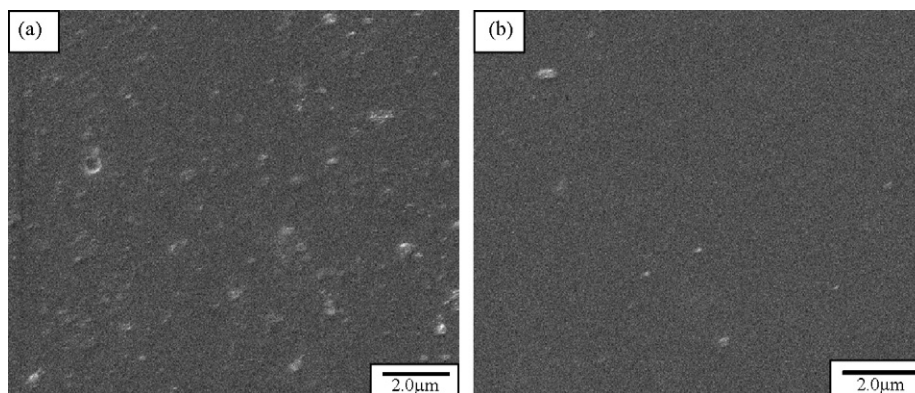


Fig. 4. The SEM images of the PS-TiO₂ (a) and PS-FePc-TiO₂ (b) films.

Fig. 7 shows the weight loss curve of different films under the sunlight exposure. The sunlight irradiation experiment was carried out twice in May–June and July, respectively. The average overall light irradiation intensity of sunlight in

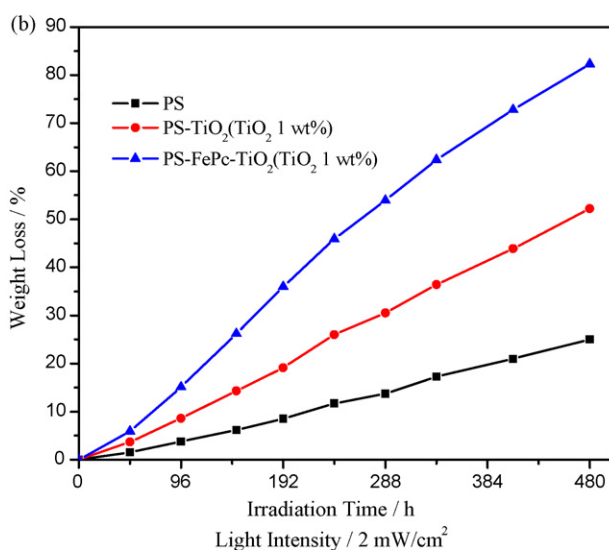
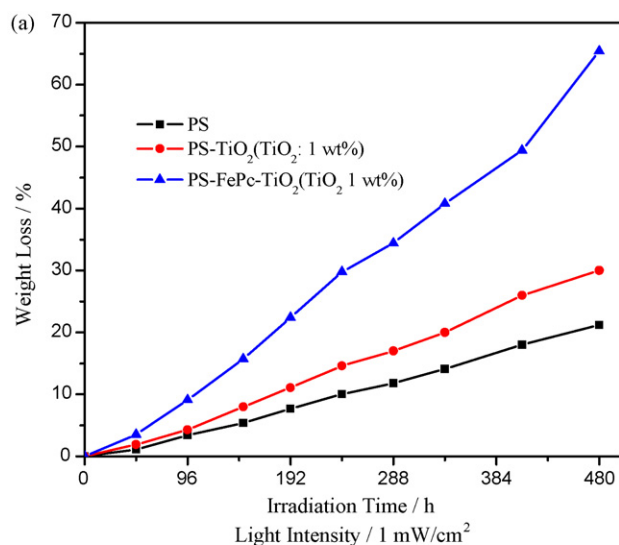


Fig. 5. Weight loss of the pure film and composite films under UV light irradiation with different light intensities (a) 1 mW/cm²; (b) 2 mW/cm².

May–June was approximate 2.8 mW/cm² (365 nm) and that in July was approximate 3.8 mW/cm². The weight loss rate of PS-FePc-TiO₂ composite film is much higher than that of the pure film and PS-TiO₂ film. The weight of pure PS film had almost no change under sunlight exposure. This result is the same as the fact that the pure PS is nondegradable in natural environment. The weight loss of PS-TiO₂ film was only 10.9% after 38 days irradiation in May–June, while that of the PS-FePc-TiO₂ film was 35% (Fig. 7a), around triple of that of the PS-TiO₂ film. The weight loss of two films was 7.7% for the PS-TiO₂ film and 20% for the PS-FePc-TiO₂ film (Fig. 7b), respectively, after 12 days irradiation in July. The weight loss of the PS-FePc-TiO₂ film was also around triple of that of the PS-TiO₂ film. It proved that PS-FePc-TiO₂ composite film had much higher photodegradable efficiency than PS-TiO₂ film under sunlight exposure in natural environment. What's more, the sunlight irradiation experiment was carried out in the quartz vessel, which was isolated from the water, rain, fog and dew, etc. The former discussion has already indicated that the presence of water vapor can improve the photodegradation efficiency. So we may deduce that the PS-FePc-TiO₂ composite film could decompose rapidly when straightly exposed in the natural environment.

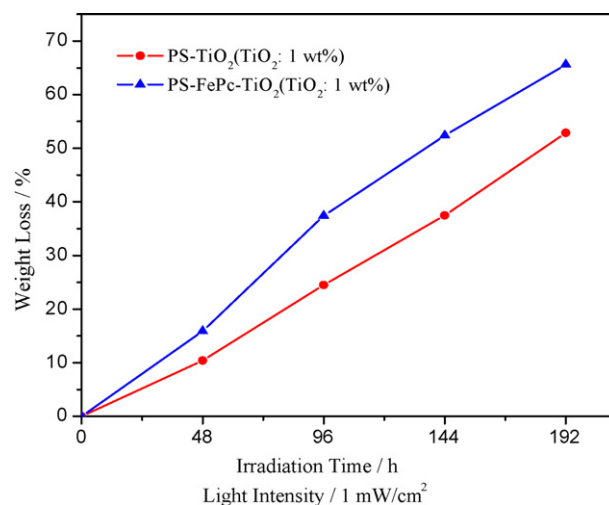


Fig. 6. Weight loss of the composite films under UV light irradiation in humidified air.

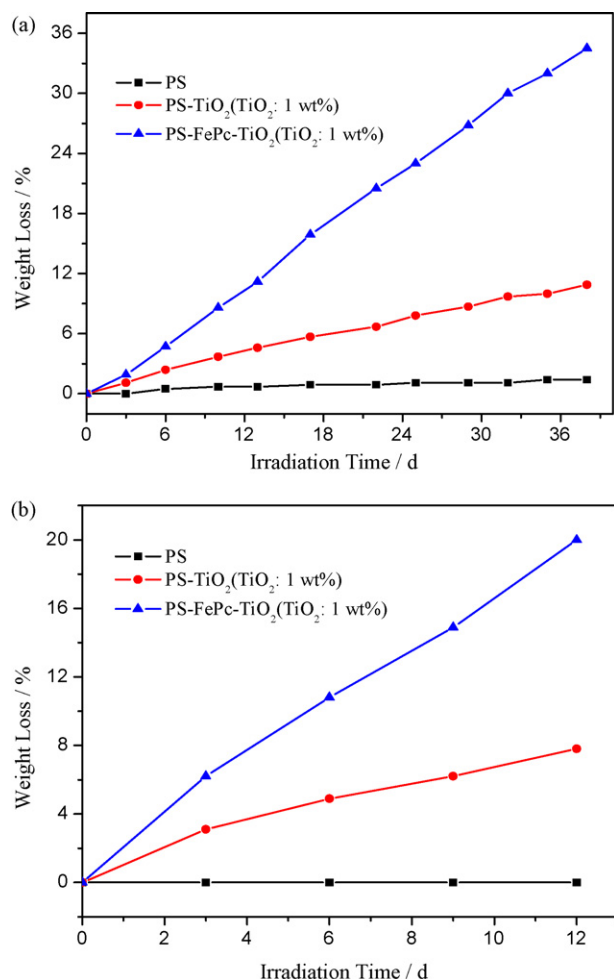


Fig. 7. Weight loss of the pure film and composite films under sunlight irradiation (a) irradiation in May–June; (b) irradiation in July.

3.4. The surface morphology of the films after photodegradation

As shown in Fig. 8, scanning electron microscope was carried out to observe the surface morphology of the films with photodegradation. Both the surface of PS, PS-TiO₂ and PS-FePc-TiO₂ composite film are smooth before irradiation (Fig. 4). The PS film has few changes except some surface chalking phenomenon after 100 h UV-irradiation (Fig. 8a). However, some big cavities around the TiO₂ nanoparticles in the composite films are observed in the identical experiment. Especially, the surface of the PS-FePc-TiO₂ film is decomposed after 100 h irradiation (Fig. 8d). The cavities were formed not only on the surface but also inside of the film. Most of the cavities were distributed around the TiO₂ particle, which indicated that the decomposition resulted from the catalysis of TiO₂.

3.5. Spectroscopic characterization

The photocatalytic degradation of PS films was also examined by FT-IR spectroscopy. Fig. 9a shows the FT-IR

spectra of the PS-FePc-TiO₂ (TiO₂: 1%) composite films before and after irradiation for 4 and 30 h. The spectrum of the original PS-FePc-TiO₂ composite films shows the characteristic absorption peaks of phenyl ring in the region of 1490, 1448, 750 and 701 cm⁻¹, which are the same as that in pure PS film [30]. It shows that the IR spectra character of polymeric matrix is not affected by embedding TiO₂ particles [31]. There is a new absorption peak in the region of 1720 cm⁻¹ after irradiation, which is the characteristic absorption of carbonyl (C=O) group. The peaks in the region of 1490, 1448, 750 and 701 cm⁻¹, which are the characteristic peaks of phenyl ring, decrease gradually with the increase of irradiation time. Both the formation of the carbonyl groups and the decrease of intensity of phenyl ring suggest that the photo-oxidized reaction has taken place in the composite film [32,33].

Fig. 9b is the FT-IR spectra of the different films after 30 h irradiation. It shows that the intensity of carbonyl(C=O) group in PS-FePc-TiO₂ film is the strongest in the three kinds of films. However, the intensity of phenyl ring characteristic peaks in PS-FePc-TiO₂ is much weaker than those in the PS-TiO₂ film and pure PS film. And those in the PS-TiO₂ film are weaker than that in pure PS film, in which phenyl ring characteristic peaks have almost no change. These all indicate that the TiO₂ catalyst makes the photodegradation of PS film more effective and FePc-TiO₂ has a higher catalytic activity than the untreated-TiO₂.

3.6. Mechanism discussion

We have known that the reaction of PS under ultraviolet irradiation occurs via direct absorption of photons by the PS macromolecule, which creates excited states, and leads to chain scission, branching cross-linking and oxidation reactions [34]. For the PS-TiO₂ composite film, there is not only the photolytic reaction of PS but also the photocatalytic reaction of PS on the surface of TiO₂. The photocatalytic reaction mechanism of PS-TiO₂ has been researched in some former works [7,8]. TiO₂ particles that absorb light with energy higher than 3.2 eV generate electron/hole pairs in the conduction band (CB) and valence band (VB), respectively. The electrons can be captured by adsorbed oxygen molecules to form O₂^{•-}. At the same time, photogenerated holes are trapped by water adsorbed on the surface to produce [•]OH. The O₂^{•-} and [•]OH are two very important reactive oxygen species for the photocatalytic degradation of PS. The active radicals described above initiate the solid-phase photocatalytic degradation of PS-TiO₂ composite film by attacking neighboring polymer chains and form carbon-centered radicals such as -(CH₂[•]CPh)- and -([•]CHCPh)-. Their successive reactions produce hydroxyl derivatives and carbonyls intermediates, resulting in polymer chain cleaved and CO₂ evolution. So the O₂ and H₂O adsorbed on the surface play the important roles in photocatalytic reactions. Our results also revealed this. The PS-TiO₂ composite films were nearly nondegradable under the Argon atmosphere in our earlier research [10]. This was also a proof that oxygen played the key role

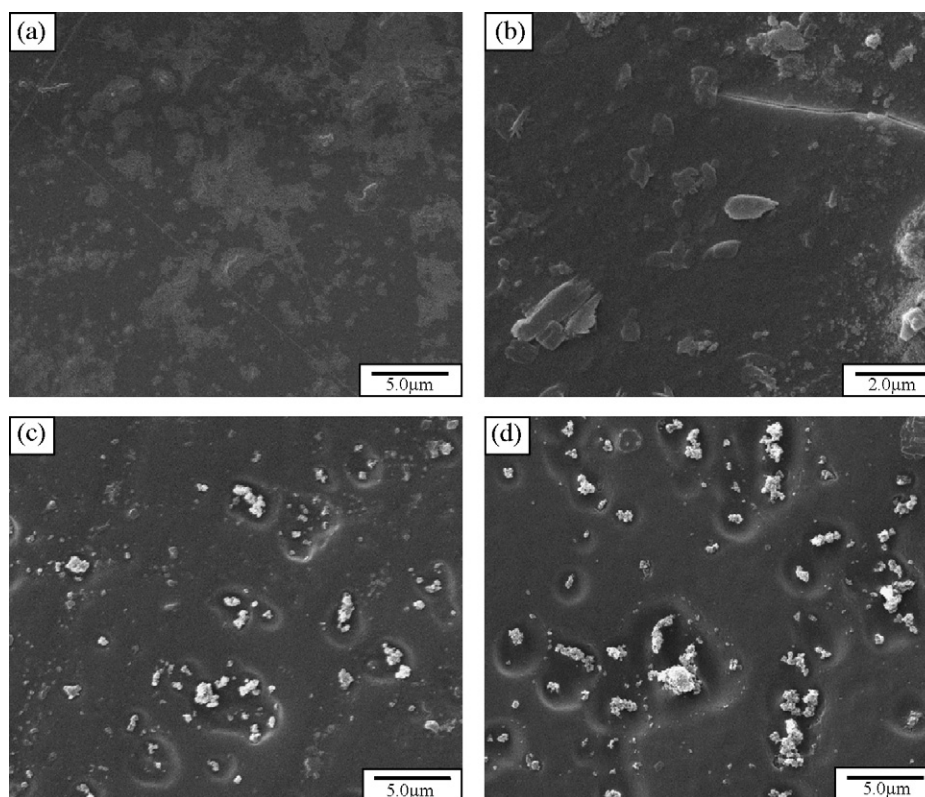


Fig. 8. The SEM images of the polymer films after irradiation with 1 mW/cm^2 UV light intensity (a) the pure PS film after 100 h irradiation; (b) the PS-TiO₂ film after 100 h irradiation; (c) the PS-FePc-TiO₂ film after 50 h irradiation; (d) the PS-FePc-TiO₂ film after 100 h irradiation.

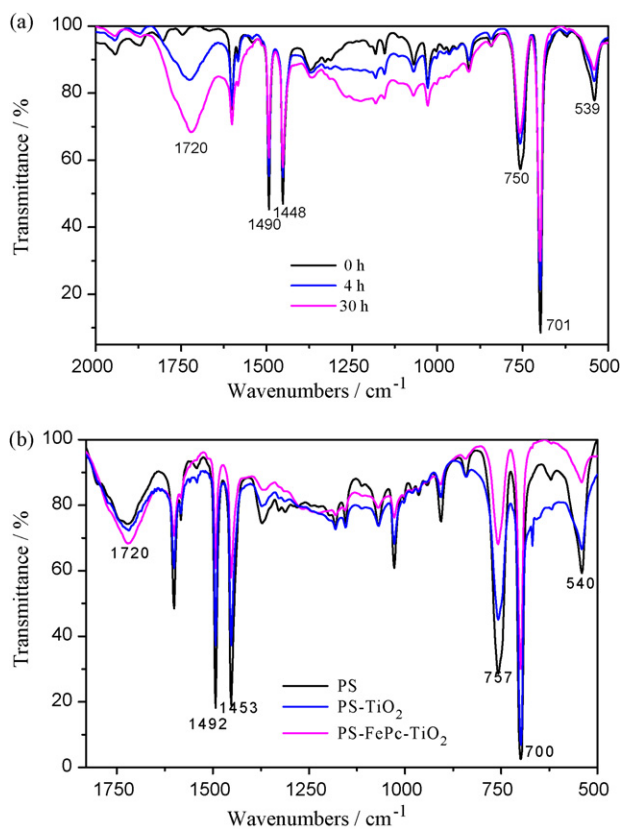


Fig. 9. FT-IR spectra of the polymer films before and after irradiation (a) the PS-FePc-TiO₂ (TiO₂: 1 wt%) composite films before and after irradiation for 4 and 30 h; (b) the different films after the identical 30 h irradiation.

in photocatalytic reaction. The result that PS-TiO₂ composite films had a higher degradable efficiency in an abundance of water vapor showed that water adsorbed the surface also played an important role. So we deem that the composite film can decompose rapidly when straightly exposed in the natural environment with abundant O₂ and water vapor.

In the absence of the electron and hole scavengers, most of them recombine with each other within a few nanoseconds. If the scavengers or surface defects are present to trap the electron or hole, electron-hole recombination can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced [7]. When the PS-FePc-TiO₂ film was irradiated by the UV light, TiO₂ was excited to generate electron/hole pairs. A hole injection from the valence band of TiO₂ to the ground state of FePc was permitted at the interface between TiO₂ and FePc, which efficiently separated the electron and hole and prevented the electron-hole recombination. This is the primary reason that the PS-FePc-TiO₂ film can degrade better than the PS-TiO₂ film even if under the UV irradiation.

From the result of the UV-vis diffuse reflectance spectra of the FePc-TiO₂ composite powder, we can see the FePc-TiO₂ composite exhibits remarkable absorbance in visible region beyond 400 nm. When the PS-FePc-TiO₂ film is irradiated by the visible light, the FePc is firstly excited to generate an electron in excited singlet state of FePc and a hole in ground state of FePc. Then the electron is injected into the conduction band of TiO₂ and a series of oxidation-reduction reactions take

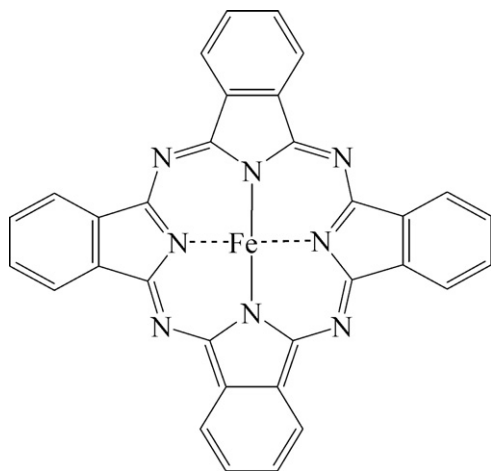
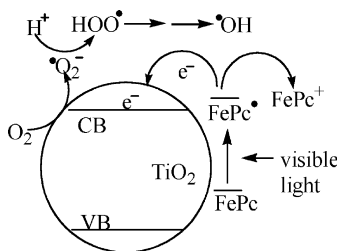


Fig. 10. The structure of FePc molecule.

place. The possible light excited process can be displayed as follows:



The dye sensitization of TiO_2 extends the light absorption to the visible spectral region. This is the major reason that the PS-FePc- TiO_2 composite film has higher efficiency under the sunlight irradiation.

In addition, the uniform dispersion of the FePc- TiO_2 nanoparticles in PS matrix is also the reason that the photocatalytic efficiency is higher for the PS-FePc- TiO_2 film than that of the PS- TiO_2 film. When the untreated TiO_2 particles were embedded into the polymer, they also aggregated and formed floccules of a few micrometers (see Fig. 4). The existence of agglomerates would decrease the interface area between polymer and the photocatalyst, resulting in a low efficiency of photocatalytic degradation. FePc is a big ring compound consisted of 57 atoms as presented in Fig. 10. The molecule position is such that its symmetry axes led along the mirror axis of an isoindole unit of FePc cover with the unit cell diagonals [35]. It forms an interconnecting network of FePc with TiO_2 nanoparticle such as the TiO_2 particle modified by organic reagent and reduced the polarity of the TiO_2 particle. Farther more, it forms of bulk hetero junction between the composite and PS polymer chain, so that the TiO_2 -FePc composites get a high stability and a uniform dispersion in PS matrix [36].

4. Conclusions

The surface modification of TiO_2 by FePc shows a high photocatalytic activity under visible light. The TiO_2 modified

by FePc has a better dispersion in PS polymer and can absorb the visible light. So the PS-FePc- TiO_2 film has much higher degradation efficiency not only under UV-irradiation but also under the sunlight irradiation, compared with the pure PS film and PS- TiO_2 film. It is a novel way to produce the photodegradable plastics.

Acknowledgment

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